
Implementation of Atomic Basis Set Composed of 1s Gaussian and 1s Slater-Type Orbitals to Carry Out Quantum Mechanics Molecular Calculations

J. C. CESCO,¹ C. C. DENNER,² G. O. GIUBERGIA,² A. E. ROSSO,²
J. E. PÉREZ,³ F. S. ORTIZ,³ O. E. TAURIAN,³ R. H. CONTRERAS⁴

¹*Instituto de Matemática Aplicada, UNSL-CONICET, San Luis, Argentina*

²*Departamento de Matemática, F.C.E.F-Q.yN., Universidad Nacional de Río Cuarto, Río Cuarto, Argentina*

³*Departamento de Química y Física, F.C.E.F-Q.yN., Universidad Nacional de Río Cuarto, Estafeta Postal No. 9 (5800), Río Cuarto, Argentina*

⁴*Departamento de Física, F.C.E.yN., Universidad Nacional de Buenos Aires, Buenos Aires, Argentina*

Received 6 August 1998; accepted 23 November 1998

ABSTRACT: A mixed atomic basis set formed with 1s Slater-type orbitals and 1s floating spherical Gaussian orbitals is implemented. Evaluation of multicenter integrals is carried out using a method based on expansion of binary products of atomic basis functions in terms of a complete basis set, and a systematic analysis is performed. The proposed algorithm is very stable and furnishes fairly good results for total energy and geometry. An LCAO-SCF test calculation is carried out on LiH. The trends observed show that there are some combinations of mixed orbitals that are appropriate to describe the system. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 604–609, 1999

Correspondence to: J. E. Pérez; e-mail: eperez@exa.unrc.edu.ar

Contract/grant sponsors: Se.C.yT. (UNRC); CONICOR;
CONICET

Keywords: atomic basis set; Slater orbitals; floating spherical Gaussian orbitals; complete functions set; Bessel functions

Introduction

In molecular calculations within the self-consistent-field linear combinations of atomic orbitals (SCF-LCAO) approach the introduction of atomic Slater-type orbitals (STO)¹ and floating spherical Gaussian orbitals (FSGO)² has proven useful. These two models can provide the Hartree–Fock limit (HFL).^{3,4} However, the number of functions required is usually very high. In effect, the STOs require the use of “d” and “f” functions to approach the HFL and, for FSGO, they require many variational parameters (localization and size of the floating orbitals, etc.) to furnish similar results.

In this work, we investigate the mixing of both types of orbitals to determine whether it is possible to reduce the complications of each type of orbital while retaining the accuracy they offer.

Here the simplest combination of STO and FSGO is presented, namely the mixture of only 1s-type functions of both kind of orbitals. The application is performed on a very well-known system, lithium hydride, for which there are numerous and very accurate results.⁵

In previous articles,^{6,7} expansions for binary products of any given class of atomic orbitals were found by using an appropriate complete function set. Therefore, it is an alternative tool^{8,9} to evaluate multicenter bielectronic integrals.

The series expansions presented in refs. 6 and 7 are also a promising tool for using a “mixed” basis set, namely, a basis set built up of different types of atomic orbitals. One of the main objectives of this work is to use an approach similar to that presented in ref. 7 to evaluate the SCF-LCAO wave function for LiH. The present atomic basis set consists of 1s STOs centered at the site of the nuclei and of FSGOs to reinforce the description of the internal shell and the bond (in general, they also describe the rear lobes and lone pairs). To compare the quality of results given by the present approach, total energies and bond length obtained are compared with those of different basis sets^{3,4} and with calculations performed using the GAUSSIAN-94 system.¹⁰

Method of Calculation

Implementation of the mixed-type AO basis set follows the main strategies delineated in previous work.⁷ To carry out the SCF calculation¹¹ a code was written in GAUSSIAN 386i programming language; all nonlinear parameter optimizations were carried out with its OPTIMUM subroutine (provided with the package). The evaluation of the necessary matrix elements (i.e., $S_{\mu\nu}$ [overlap], $T_{\mu\nu}$ [kinetic energy], $V_{\mu\nu}$ [nuclear–electron attraction], and $(\mu\nu|\rho\sigma)$ [bielectronic integrals]), owing to their multicenter character, was naturally divided into an analytical and a numerical approach.

All quantities that depend only on the binary products of GTOs¹¹ have a direct computation. Those integrals that depend only on the binary products of STOs, such that they include the monocentric and bicentric $S_{\mu\nu}$, $T_{\mu\nu}$, $V_{\mu\nu}$, and $(\mu\nu|\rho\sigma)$, are also amenable to straightforward evaluation.¹² On the other hand, all three- and four-center bielectronic integrals are obtained with the Fourier–Dini–Bessel (FDB), method described previously,^{6,7} which includes expansions. Thus, in this approach, a bielectronic integral $(\mu\nu|\rho\sigma)$ is approximated by the following partial sum $PS(L, N; R)$:

$$PS(L, N; R) = 4\pi \sum_{l=0}^L \sum_{m=-l}^l \sum_{n=1}^N \frac{\Gamma_{lmn}^{\mu\nu*} \Gamma_{lmn}^{\rho\sigma}}{k_{ln}^2} \quad (1)$$

where:

$$\Gamma_{lmn}^{\mu\nu} = \int dV \phi_{\mu}(\underline{r} - \underline{R}_{\mu}) \phi_{\nu}(\underline{r} - \underline{R}_{\nu}) U_{lmn}^*(\underline{r}) \quad (2)$$

with:

$$U_{lmn}(\underline{r}) = Y_{lm}(\theta, \varphi) B_{ln} J_{l+1/2}(k_{ln}r)/r^{1/2} \quad (3)$$

and $\phi_{\mu}(\underline{r} - \underline{R}_{\mu})$ is the AO centered at \underline{R}_{μ} and $Y_{lm}(\theta, \varphi)$ is the normalized spherical harmonic; $J_{l+1/2}(v)$ is a Bessel function of half-integer order with normalization constants B_{ln} ; k_{ln} are such that $J_{l-1/2}(k_{ln}R) = 0$.

No special treatment is needed for the binary products that mix a GTO (ϕ_{ν}) with a STO (ϕ_{μ}) in the $\Gamma_{lmn}^{\mu\nu}$ coefficients,⁷ and their final expressions

are given in terms of unidimensional integrals:

$$\begin{aligned} \Gamma_{lmn}^{\mu\nu} &= N_\mu N_\nu \int dV \exp(-\alpha_\mu |r - \underline{R}_\mu|) \\ &\quad \times \exp(-\beta_\nu |r - \underline{R}_\nu|^2) U_{lmn}^*(r) \\ &= N_\mu N_\nu (\alpha_\mu 0.5/\pi^{1/2}) \int_0^\infty ds s^{-3/2} \left(\frac{\pi}{s + \beta_\nu} \right)^{3/2} \\ &\quad \times \exp\left(-\frac{s\beta_\nu}{s + \beta_\nu} |\underline{R}_\mu - \underline{R}_\nu|^2 - \frac{k_{ln}^2}{4(s + \beta_\nu)} \right) \\ &\quad \times \exp(-\alpha_\mu^2/4s^2) U_{lmn}^* \left(\frac{s\underline{R}_\mu + \beta_\nu \underline{R}_\nu}{s + \beta_\nu} \right) \\ &= N_\mu N_\nu (16\pi) \int_0^\infty dy y^3 (\alpha_\mu^2 + 4\beta_\nu y^2)^{-3/2} \\ &\quad \times \exp\left(-y^2 - \frac{k_{ln}^2 y^2}{\alpha_\mu^2 + 4\beta_\nu y^2} \right. \\ &\quad \left. + \frac{\alpha_\mu^2 \beta_\nu}{\alpha_\mu^2 + 4\beta_\nu y^2} |\underline{R}_\mu - \underline{R}_\nu|^2 \right) \\ &\quad \times U_{lmn}^* \left(\frac{\alpha_\mu^2 \underline{R}_\mu + 4\beta_\nu y^2 \underline{R}_\nu}{\alpha_\mu^2 + 4\beta_\nu y^2} \right) \end{aligned} \tag{4}$$

where $y = \alpha_\mu^2/4s^2$ and N_μ and N_ν are normalization constants for ϕ_μ and ϕ_ν , respectively. Table I shows that the numerical behavior of the partial sums is analogous to that found for the corre-

sponding STOs.⁷ All one- and two-center bielectronic integrals that mix both kinds of AOs are calculated using eq. (1). It is worthy of mention that the evaluation of $S_{\mu\nu}$, $T_{\mu\nu}$, and $V_{\mu\nu}$, which also involves Gaussian and Slater orbitals, follows a scheme completely analogous to that of eq. (4); owing to the factor “exp(−y²)” in their integrands, the corresponding upper limits of integration were fixed at 10.

The value $R = 5$ a.u. remained fixed in all calculations because this choice generates an error ($\leq 5 \cdot 10^{-4}$ a.u.) that is smaller than that of the present model introduced with respect to the HFL.

The integration points used to evaluate the $\Gamma_{lmn}^{\mu\nu}$ coefficients were fixed at 40 (Gauss–Legendre quadrature), because pilot calculations showed no appreciable variations in significant values, such as in ref. 7.

Results and Discussion

The study of the LiH molecule, with the mixed atomic basis sets, was carried out by considering the basis of Figure 1. In this figure, “.” represents a 1s STO with an orbital exponent α and its position, where the orbital is located in the molecule. Similarly, “×” represents a 1s GTO with an orbital exponent β , “○” represents a nucleus, and “⊗” indicates a 1s GTO centered on a nucleus.

TABLE I.
Bielectronic Integrals Evaluated Using Partial Sums of Eq. (1) Corresponding to B7 Basis.^a

<i>R</i> ^b	<i>L</i>	<i>N</i>	(24 55)	(16 45)	(15 26)	(15 22)	(12 34)	(24 24)
4	10	10	0.2822223	0.0368662	0.1983937	0.1959285	0.0114501	0.4915474
	15	15	0.2822223,	0.0368662	0.1983927	0.1959224	0.0114501	0.4915475
	25	25	0.2822223	0.0368662	0.1983927	0.1959226	0.0114501	0.4915475
	30	30	0.2822223	0.0368662	0.1983927	0.1959226	0.0114501	0.4915475
5	10	10	0.2822284	0.0368662	0.1983946	0.1959877	0.0114501	0.4924468
	15	15	0.2822284	0.0368662	0.1983937	0.1959819	0.0114501	0.4924471
	25	25	0.2822284	0.0368662	0.1983937	0.1959822	0.0114501	0.4924471
	30	30	0.2822284	0.0368662	0.1983937	0.1959822	0.0114501	0.4924471
6	10	10	0.2822284	0.0368662	0.1983946	0.1959903	0.0114501	0.4924614
	15	15	0.2822284	0.0368662	0.1983937	0.1959849	0.0114501	0.4924619
	25	25	0.2822284	0.0368662	0.1983937	0.1959851	0.0114501	0.4924619
	30	30	0.2822284	0.0368662	0.1983937	0.1959851	0.0114501	0.4924619

^a Here (*ij|pq*) means $(\phi_i \phi_j | \phi_p \phi_q) = \int dV_1 dV_2 [(\phi_i \phi_j)(1)(\phi_p \phi_q)(2)] / r_{12}$, where: ϕ_1 refers to the STO on the Li, ϕ_2 refers to the STO on the H; ϕ_3 refers to the GTO on the Li, ϕ_4 refers to the GTO on the H; ϕ_5 refers to the GTO below the Li and ϕ_6 refers to the GTO above the Li.
^b Parameter R is associated with the complete set $U_{lmn}(r)$; $L = (l)_{\max}$ and $N = (n)_{\max}$, where l and n are the sum indexes in eq. (1).

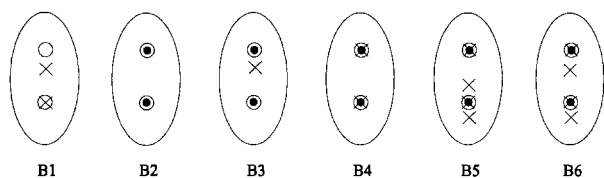


FIGURE 1. Different basis sets considered in this work. The Bi, with i ranging from 1 to 6, refers the particular basis set. Symbols: (○) nucleus; (●) 1s STO; (×) 1s GTO. Lower nucleus is Li and the upper nucleus is H.

The B1 and B2 basis sets are the simplest choice. The energies and bond length values are given in Table II. It is worth noting that, although these basis sets are very small, B2 gives much better values, particularly in regard to bond length. Analysis of cases B1 and B2 suggests that the B3 basis set would constitute a natural improvement. The variational theorem guarantees a lower energy value in this case. However, the position of the

Gaussian orbital seems inappropriate because an overly large internuclear distance is obtained. From comparison with B2, this effect can be associated with the fact that an extra orbital in this level of approximation allows only electrons to move in the internuclear region, making the internuclear distance to return to an unrealistic value, in order to lower the energy.

The behavior shown in B3 can be avoided; that is, an improved basis can be built by adding to B2 a GTO on each atomic nucleus forming the basis B4. Here, the orbitals remain fixed on the nuclei. The energy values obtained as well as the internuclear distance suggest that this model can be taken as a good starting point for better basis sets. This resembles the general studies performed by using 1s atomic orbitals in the currently used basis sets (double-zeta and contracted Gaussians¹¹).

To improve B4, two more GTOs are considered. First, they are forced to remain symmetric with respect to the Li nuclear center (B5 basis), resulting

TABLE II. Total Energy (E_T) and Bond Length (D) Obtained with Different Basis Sets (Bi, $i = 1, \dots, 7$) for LiH.^a

Model	$L = N$	E_T	D	α_1	α_2	β_3	β_4	β_5^5	d_5^6
B1		-6.5	3.22						
B2		7.94577	2.9832	2.68576	0.78303				
B3	10	-7.95932	3.2054	2.68848	1.04435	0.07886			2.0571
	15	-7.95944	3.2069	2.68845	1.04540	0.07895			2.0577
	25	-7.95945	3.2071	2.68844	1.04578	0.07897			2.0593
B4	15	-7.96102	3.0046	3.00745	0.80105	0.64790	0.29926		
	25	-7.96087	3.0019	3.00352	0.80104	0.64492	0.29883		
	30	-7.96086	3.0019	3.00352	0.80104	0.64492	0.29883		
B5	15	-7.98049	3.0343	2.98705	0.80068	0.62614	0.23145	0.23599	1.3695
	25	-7.98035	3.0314	2.98057	0.80093	0.61781	0.23183	0.23610	1.3707
	30	-7.98035	3.0317	2.98040	0.80073	0.61782	0.23152	0.23600	1.3708
B6	15	-7.98048	3.0019	3.00352	0.80104	0.64492	0.29883	0.64372	0.0771
								0.27353	1.9133
	25	-7.98033	3.0019	3.00352	0.80104	0.64492	0.29883	0.64352	0.0771
								0.27353	1.9133
	30	-7.98033	3.0019	3.00352	0.80104	0.64492	0.29883	0.64352	0.0771
								0.27353	1.9133
B7	15	-7.98308	3.0449	3.12000	0.80384	0.97412	0.21426	0.42941	0.3280
								0.19535	1.4256
	25	-7.98283	3.0400	3.10147	0.80371	0.93793	0.21122	0.43494	0.3639
								0.19032	1.5619
	30	-7.98282	3.0392	3.10205	0.80409	0.93828	0.21135	0.43422	0.3644
								0.18933	1.5620

^a These values are given under the variations of the L and N parameters, which define the evaluation of the bielectronic integrals. Here, α_1 (β_3) and α_2 (β_4) are the exponents of STOs (GTOs) on Li and H, respectively, except for B3, for which GTO number "3" is located above the Li nucleus distance d . Analogously, β_5 and β_6 are the exponents of GTOs located below (d_5) and above (d_6) the Li nucleus, respectively. Hartree-Fock limit: $E_T = -7.987315$ a.u. and $D = 3.034$ a.u. (ref. 3); 4-31G: $E_T = -7.977343$ a.u. and $D = 3.0803$ a.u. (ref. 10); 6-31G**: $E_T = -7.981340$ a.u. and $D = 3.236$ a.u. (ref. 10).

in a "p-like character." Then the last restriction is dropped (B6 basis). Within the B5 basis, all parameters are estimated. In the B6 basis, only the parameters corresponding to the new GTOs introduced are estimated (the others are taken from B4 with $L = N = 30$). In Table II it is shown that the results follow the expected trend. The energy values obtained for B5 and B6 are ≈ 0.02 a.u. (0.6 eV) below that of the corresponding B4 value, and the B5 internuclear distance (3.0317 a.u.) is very close to the HFL result (3.034 a.u.). Table II also shows (B7 basis) the results of a full-parameter optimization of B6, keeping two GTOs at the nuclei. These results represent the best energy value (-7.9828 a.u.) and internuclear distance (3.0392 a.u.) presented in this work, and it is stressed that they have been obtained with only six basis functions; in Figures 2, 3, and 4, the behavior of the corresponding molecular charge density [$\rho(r)$] is depicted. The whole trend confirms the relevance of achieving "a correct background" with the proposed mixed basis set (B4 in this case), from which there would be satisfactory improvements.

As a final remark, it is pointed out that the calculation performed reveals that the orbital exponents of the STOs are close to those already presented in the literature. In addition to provid-

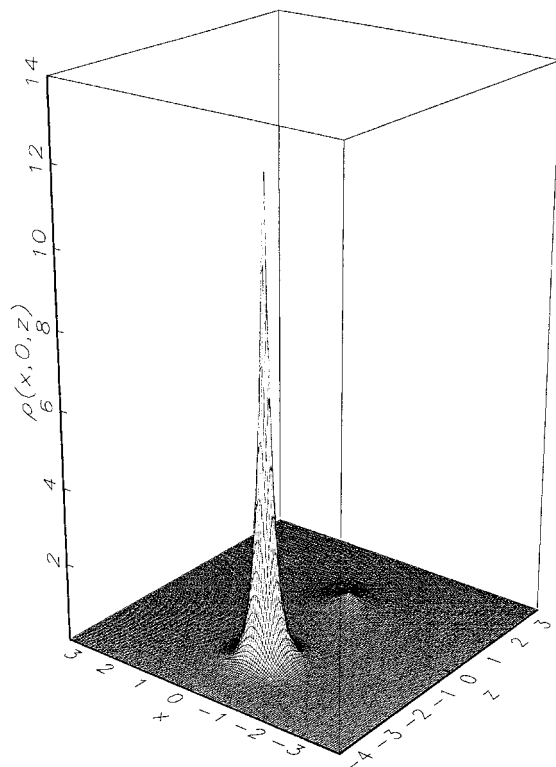


FIGURE 2. Graph of the electron density, $\rho(\mathbf{r})$ (corresponding to B7 basis), restricted to the plane that contains the nuclei (xz plane). All values given in atomic units.

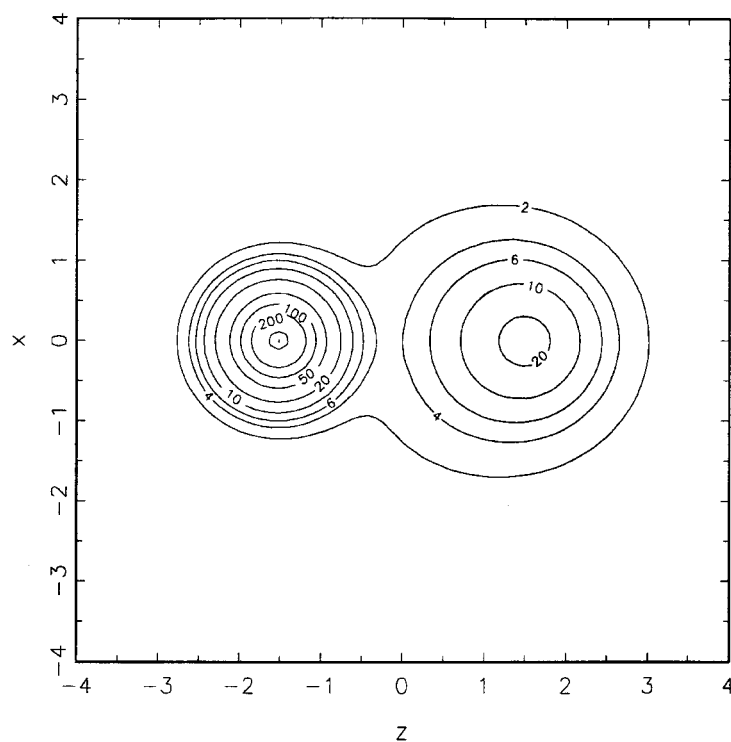


FIGURE 3. Electron density contour plot for LiH (corresponding to B7 basis). Contours are in atomic units and are multiplied by a factor 10^2 .

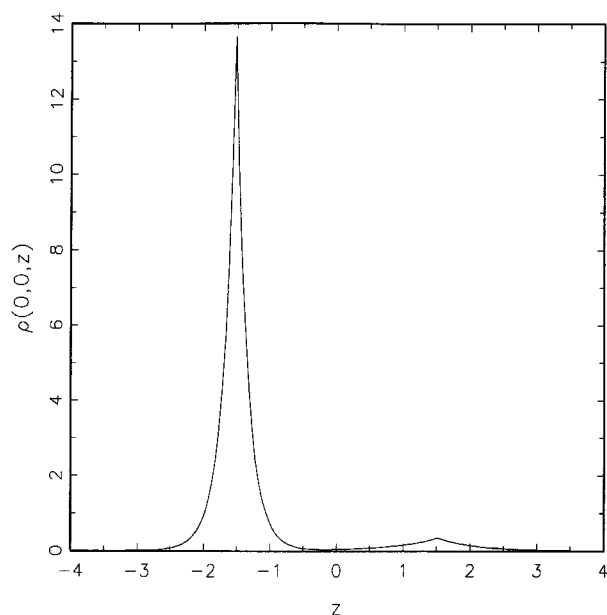


FIGURE 4. Electron-density profile (corresponding to B7 basis) along the z axis. Values given in atomic units.

ing a way to determine some heuristic rules from which orbital exponents can be chosen (in the case that the optimization is intended to be reduced), they reveal that the algorithm implemented is, in some sense, stable.

Both the basis sets (model) and the algorithm contain many possibilities. The model is able to

deal with larger and more complex systems. The algorithm actually implemented has proven to be stable, although research is ongoing to improve its numerical performance. Several alternatives for carrying out extensive computations are being attempted.

References

1. (a) Fernández Rico, J.; López, R.; Aguado, A.; Ema, I.; Ramírez, G. *J Comput Chem* 1998, 19, 1284–1293. (b) Bouferguene, A.; Fares, M.; Hoggan, L. *Int J Quantum Chem* 1996, 57, 801–810.
2. Pakiari, A.; Kaleshifard, F. M. *J Mol Struct (Theochem)* 1995, 340, 175–183.
3. Cade, P.; Huo, W. *J Chem Phys* 1967, 47, 614.
4. Pakiari, A. *J Mol Struct (Theochem)* 1995, 331, 155–167.
5. Lee, B.; Stout, J.; Dykstra, C. *J Mol Struct (Theochem)* 1997, 400, 56–68.
6. Pérez, J. E., et al. *Theor Chim Acta* 1994, 88, 147.
7. Cesco, J. C., et al. *J Comput Chem* 1995, 16, 1507.
8. Jones, H. *J Comput Chem* 1991, 12, 1217.
9. (a) Fernández Rico, J., et al. *Comput Phys Commun* 1997, 105, 216. (b) Montagnani, R.; Salvetti, O. *Int J Quantum Chem* 1993, 47, 225–229.
10. Pople, J. A., et al. *GAUSSIAN-94*, Revision D.4; Gaussian: Pittsburgh, PA; 1995.
11. Szabo, A.; Ostlund, N. *Modern Quantum Chemistry*; Macmillan: London; 1982.
12. Ruedenberg, K. *J Chem Phys* 1951, 19, 1459.